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Combustion and sublimation calorimetric studies on acetylurea and trimethyl isocyanurate^{*}

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Standard enthalpies of formation in the crystalline and gaseous states have been determined for acetylurea and trimethyl isocyanurate by oxygen bomb-combustion calorimetry and sublimation calorimetry. Derived values are as follows:

	$\frac{-\Delta_{\rm f} H_{\rm m}^{\circ}({\rm c})}{({\rm kJ}\cdot{\rm mol}^{-1})}$	$\frac{-\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})}{({\rm kJ}\cdot{\rm mol}^{-1})}$
CH3CONHCONH2 CON(CH3)CON(CH3)CON(CH3)	$544.21 \pm 0.54 \\ 677.92 \pm 0.97$	441.16±0.86 589.7 ±1.5

Stabilization energies related to intramolecular interaction between π -electrons of carbonyl groups and lone-pair electrons of adjacent nitrogen atoms have been evaluated for acetamide and urea as well as for these compounds as enthalpy changes of "isodesmic" reactions using ethane as a reagent for the cleavage of CO-N bonds and are discussed.

1. Introduction

It is well known that π -electrons of a carbonyl group in an amide strongly interact with lone-pair electrons on the adjacent nitrogen atom, providing the interconnecting C-N bond with significant double-bond character. This bond is an important one since it occurs not only in amides and ureas but also in proteins, DNA bases, and synthetic polyamides. The delocalization of π -electrons would lead to stabilization of the molecule.

In this paper, standard molar enthalpies of formation in the gaseous state at 298.15 K are reported for CH₃CONHCONH₂ (acetylurea) and

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 $CON(CH_3)CON(CH_3)CON(CH_3)$ {trimethyl isocyanurate or 1,3,5-trimethyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione}. This work was performed to obtain basic information for the study of the effect of elongation and cyclization of an alternating -CO-N- chain on the energy.

2. Experimental

Commercial acetylurea (Tokyo Kasei, G. R.) was purified by recrystallization from aqueous solution and then from ethanolic solution, followed by vacuum sublimation at 370 K and 0.2 Pa. The purified sample showed no thermal anomaly on d.s.c. curves below the melting temperature (491 K) on heating, but it decomposed on melting. To assess both the purity of the sample and the completeness of combustion, total carbon-dioxide recovery was determined in each experiment using an apparatus described elsewhere.⁽¹⁾

Trimethyl isocyanurate was synthesized from cyanuric acid according to the method of Fisher and Frank.⁽²⁾ Purification was carried out by repeated recrystallization from aqueous solutions, followed by vacuum fractional sublimation at (340 ± 10) K and 0.2 Pa. The purified sample neither showed thermal anomaly below the melting temperature (450 K) nor decomposed on melting. Purity, assessed from d.s.c. heating curves in the melting region, was 99.90 moles per cent.

An isoperibol rotating-bomb combustion calorimeter described elsewhere.^(1,3) was used without rotating the bomb. The energy equivalent of the empty calorimeter was determined by burning thermochemical standard benzoic acid (N.B.S. SRM 39i, $\Delta_c u_{cert} = -26434 \text{ J} \cdot \text{g}^{-1}$) under certificate conditions. The energy equivalent was calculated by a procedure obtained by modification of the procedure for the calculation of the standard energy of combustion of a compound,⁽⁴⁾ using $\Delta_{c}u^{\circ} = -26413._{6} \text{ J} \cdot \text{g}^{-1}$ for the benzoic acid. This value was obtained from the certified value by using the equation: $|\Delta_c u_{cert}| - |\Delta_c u^{\circ}| = 20.4 \text{ J} \cdot \text{g}^{-1}$.⁽⁵⁾ The mean and standard deviation of the mean of the observed energy equivalents were $(15165.4 \pm 0.4) \text{ J} \cdot \text{K}^{-1}$ from 12 runs and $(15165.7 \pm 0.4) \text{ J} \cdot \text{K}^{-1}$ from 10 runs for combustion-calorimetric experiments on acetylurea and trimethyl isocyanurate, respectively. Both substances were burnt at an oxygen pressure of 3.03 MPa in the presence of 2 g (for acetylurea) or 3 g (for trimethyl isocyanurate) of water in the combustion bomb. For acetylurea, a pellet of the thermochemical standard benzoic acid ($\Delta_c u^\circ = -26413_6 \text{ J} \cdot \text{g}^{-1}$), weighing about 0.37 g, was used as an auxiliary material to avoid soot formation. No carbon monoxide was detected from bomb gas after any experiment. Nitric acid was determined by titration with aqueous sodium hydroxide.

A sublimation calorimetric system using a Calvet microcalorimeter with apparatus II and container $C^{(6)}$ was employed. Measurements were carried out in the ranges 360 to 407 K and 330 to 360 K for acetylurea and trimethyl isocyanurate, respectively.

The experimental results are based on relative atomic masses recommended by IUPAC (1979).⁽⁷⁾ The density ρ , specific heat capacity c_p , and specific compression energy $(\partial u/\partial p)_T$ at 298.15 K, used for correction of weighings in air to masses and

Material	Formula	$\frac{\rho}{\mathbf{g}\cdot\mathbf{cm}^{-3}}$	$\frac{c_p}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{g}^{-1}}$	$\frac{-(\partial u/\partial p)_T}{\mathbf{J}\cdot\mathbf{MPa}^{-1}\cdot\mathbf{g}^{-1}}$	
Benzoic acid	$C_7H_6O_2$	1.32	1.21	0.12	
Fuse	CH1.86O0 93	1.50	1.70	0.29	
Acetylurea	$C_{1}H_{6}O_{2}N_{2}$	1.37	(1.21)	(0.12)	
Trimethyl isocyanurate	$C_3H_9O_3N_3$	1.35	(1.21)	(0.12)	

TABLE 1. Auxiliary quantities used in the calculations. Estimated values are parenthesized

reduction of experimental results to the standard state,[†] are shown in table 1. Other auxiliary quantities were $V(\text{bomb}) = 0.3469 \text{ dm}^3$ and $\Delta_c u^{\circ}(\text{fuse}) = -16507 \text{ J} \cdot \text{g}^{-1}$.

3. Results

Detailed results of combustion-calorimetric experiments are presented in tables 2 and 3 for acetylurea and trimethyl isocyanurate, respectively. The symbols in these tables are essentially those used by Hubbard *et al.*⁽⁴⁾ Molar standard energies of combustion refer to the idealized reactions at 298.15 K:

$$C_{a}H_{b}O_{c}N_{d}(c) + \{(4a+b-2c)/4\}O_{2}(g) = aCO_{2}(g) + (b/2)H_{2}O(l) + (d/2)N_{2}(g).$$
 (1)

The mean and standard deviation of the mean of the observed standard energies of combustion were $-(1495.05\pm0.16) \text{ kJ} \cdot \text{mol}^{-1}$ and $-(2971.24\pm0.24) \text{ kJ} \cdot \text{mol}^{-1}$, for acetylurea and trimethyl isocyanurate, respectively. Those of observed total carbon dioxide recoveries were (0.9999±0.0002) for acetylurea.

Detailed results of sublimation calorimetric experiments are presented in table 4. The standard molar enthalpy of sublimation was calculated by the equation: $\Delta_{sub} H^{\circ}_{m}(T) = (M/m)E_{calib} \times (S_{T}/S_{B})$, where M and m are the molar mass and the

† In this paper, the standard pressure is 101 325 Pa.

TABLE 2. Combustion calorimetric results of acetylurea; $r(CO_2)$ is the ratio of CO₂ found to CO₂ expected

1.20096	1.19948	1.20213	1.20078	1.20204	1.20141
0.36797	0.36701	0.36676	0.36664	0.36670	0.36778
0.00218	0.00217	0.00221	0.00217	0.00222	0.00214
23.17908	23.18324	23.17395	23.17364	23.17255	23.17302
25.00570	25.00754	25.00065	24.99853	24.99843	25.00046
0.01944	0.01968	0.02010	0.01979	0.01923	0.01987
2.21	2.38	2.19	2.36	2.47	2.38
22.1	21.4	21.4	21.5	21.4	21.4
86.6	89.5	89.5	80.7	83.0	86.6
21.9	21.9	21.9	21.9	21.9	21.9
23.9	23.8	23.8	23.8	23.8	23.8
27.4440	27.4051	27.4351	27.4123	27.4357	27.4498
14.6395	14.6434	14.6409	14.6487	14.6489	14.6428
1494.58	1494.98	1494.72	1495.52	1495.54	1494.93
0.9999	1.0000	1.0000	1.0002	0.9996	1.0000
	1.20096 0.36797 0.00218 23.17908 25.00570 0.01944 2.21 22.1 86.6 21.9 23.9 27.4440 14.6395 1494.58 0.9999	1.20096 1.19948 0.36797 0.36701 0.00218 0.00217 23.17908 23.18324 25.00570 25.00754 0.01944 0.01968 2.21 2.38 22.1 21.4 86.6 89.5 21.9 23.9 23.9 23.8 27.4440 27.4051 14.6395 14.6434 1494.58 1494.98 0.9999 1.0000	1.20096 1.19948 1.20213 0.36797 0.36701 0.36676 0.00218 0.00217 0.00221 23.17908 23.18324 23.17395 25.00570 25.00754 25.00256 0.01944 0.01968 0.02010 2.21 2.38 2.19 22.1 21.4 21.4 86.6 89.5 89.5 21.9 21.9 21.9 23.9 23.8 23.8 27.4440 27.4051 27.4351 14.6395 14.6434 14.6409 1494.58 1494.98 1494.72 0.9999 1.0000 1.0000	1.20096 1.19948 1.20213 1.20078 0.36797 0.36701 0.36676 0.36664 0.00218 0.00217 0.00221 0.00217 23.17908 23.18324 23.17395 23.17364 25.00570 25.00754 25.00065 24.99853 0.01944 0.01968 0.02010 0.01979 2.21 2.38 2.19 2.36 22.1 21.4 21.4 21.5 86.6 89.5 89.5 80.7 21.9 21.9 21.9 21.9 23.9 23.8 23.8 23.8 27.4440 27.4051 27.4351 27.4123 14.6395 14.6434 14.6409 14.6487 1494.58 1494.98 1494.72 1495.52 0.9999 1.0000 1.0000 1.0002	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

m(compd)/g	1 56208	1 56380	1 561 39	1 55664	1 55959	1 56065
m(fuse)/g	0.00224	0.00222	0.00215	0.00214	0.00229	0.00212
$(T_i/K) - 273.15$	23.18296	23.18229	23.18558	23.19091	23.18788	23.18632
$(T_{\rm f}/{\rm K}) - 273.15$	24.99760	24.99903	24.99928	24.99984	24.99925	24.99913
$\Delta T_{\rm corr}/{\rm K}$	0.01910	0.01852	0.01833	0.01855	0.01862	0.01854
$\Delta U_{\rm ign}/{\rm J}$	1.68	2.38	2.48	2.86	2.91	2.13
$\Delta U_{\Sigma}/J$	20.6	20.5	20.5	20.4	20.6	20.6
$\Delta_{dec} U(HNO_3)/J$	106.9	114.4	110.4	109.8	103.1	103.2
$\varepsilon^{i}(\text{cont})/(\mathbf{J}\cdot\mathbf{K}^{-1})$	26.0	26.0	26.0	26.0	26.0	26.0
$\varepsilon^{f}(\text{cont})/(\mathbf{J}\cdot\mathbf{K}^{-1})$	27.7	27.7	27.7	27.7	27.7	27.7
$-\Delta_{IBP}U/kJ$	27.2759	27.3158	27.2723	27.1961	27.2321	27.2560
$-{\Delta_{\rm c} U_{\rm m}/M}/{({\rm kJ}\cdot{\rm g}^{-1})}$	17.3560	17.3579	17.3602	17.3648	17.3576	17.3627
$-\Delta_{\rm c} U_{\rm m}/({\rm kJ\cdot mol^{-1}})$	2970.58	2970.90	2971.29	2972.08	2970.84	2971.73

TABLE 3. Combustion calorimetric results of trimethyl isocyanurate

TABLE 4. Details of sublimation calorimetric results on acetylurea and trimethyl isocyanurate. T, Temperature of experiment; d, diameter of effusion orifice (length: 1.0 mm); t, time spent for effusion; m, mass lost during the effusion; E_{calib} , electric energy used in the calibration; S_T/S_B , the ratio of nett area to the area of calibration; $^{(6)} \Delta_{sub} H^{\circ}_m(T)$, standard molar enthalpy of sublimation

$\frac{\frac{1}{K}}{\frac{m}{mm}} = \frac{\frac{1}{ks}}{\frac{m}{mg}} = \frac{\frac{1}{K}}{\frac{1}{K}} = \frac{\frac{1}{K}}{\frac{1}{K}} = \frac{\frac{1}{K}}{\frac{1}{K}} = \frac{\frac{1}{K}}{\frac{1}{K}} = \frac{\frac{1}{K}}{\frac{1}{K}} = \frac{1}{K} = \frac{1}{K}$	$\frac{1}{1}$							
K mm ks mg J S _B kJ·mc	51							
A	51							
A 0071/111800	51							
Acetylurea	51							
360.5 1.0 4.7 19.88 2.814 0.915 102.0								
360.5 1.0 16.2 68.80 3.021 22.902 102.0	57							
369.1 1.0 42.6 40.35 18.159 2.225 102.2	26							
369.1 1.0 84.0 77.53 17.872 4.361 102.0	53							
369.1 1.0 87.2 78.21 19.633 3.996 102.4	41							
369.2 1.0 97.8 100.94 84.628 1.197 102.4	42							
369.2 1.0 20.0 20.70 8.233 2.522 102.4	42							
369.3 1.0 32.0 35.23 16.198 2.176 102.1	14							
384.4 1.0 16.5 46.75 21.641 2.171 102.5	59							
384.4 1.0 19.2 76.89 28.039 2.742 102.0)7							
406.8 0.3 70.3 140.55 102.953 1.365 102.0)6							
407.2 0.3 70.8 140.95 26.957 5.234 102.3	20							
Trimethyl isocyanurate								
330.1 1.0 18.3 16.06 2.146 3.794 86.7	79							
330.2 1.0 81.4 74.67 7.597 5.018 87.3	39							
360.2 0.3 86.8 88.15 8.214 5.366 85.5	58							
360.3 0.3 81.4 82.01 8.820 4.694 86.4	41							
360.3 0.3 82.6 81.40 9.319 4.362 85.4	17							
360.0 0.3 76.6 77.45 5.236 7.445 86.1	5							
346.0 1.0 18.0 77.65 15.106 2.598 86.5	52							
346.0 1.0 17.0 70.32 13.986 2.537 86.3	36							
346.1 1.0 17.9 74.52 15.292 2.449 86.0)6							
346.1 1.0 17.7 70.99 16.411 2.179 86.2	22							
346.2 1.0 22.5 88.62 17.530 2.549 86.2	29							



FIGURE 1. Sublimation enthalpy against temperature (a) of acetylurea and (b) of trimethyl isocyanurate. \bigcirc , Observed values; \bigcirc , the values at 298.15 K. Upper and lower curves show the 95 per cent confidence limits.

mass of sample lost during effusion, respectively, E_{calib} the electric energy used for calibration, and (S_T/S_B) the ratio of nett area to area of calibration.⁽⁶⁾

The observed values are plotted against temperature in figure 1. The values at 298.15 K were estimated by extrapolation based on the linear-regression analysis of experimental results.⁽⁸⁻¹⁰⁾

Derived standard thermodynamic quantities are presented in table 5. CODATA key values for thermodynamics⁽¹¹⁾ were used to derive these values. Uncertainties are twice the final overall standard deviation of the mean.⁽¹²⁾

4. Discussion

No previous determination of enthalpies of combustion or of sublimation was found in the literature for the present compounds. Standard enthalpies of formation determined by other methods were not found in the literature.

As a method of empirical evaluation of the magnitude of energetic stabilization for acetamide and urea as well as the present compounds, standard enthalpy changes of the following gas-phase reactions at 298.15 K were examined:

$$CH_{3}CONH_{2} + CH_{3}CH_{3} = CH_{3}COCH_{3} + CH_{3}NH_{2};$$

$$\Delta_{r}H_{m}^{\circ} = (81.8 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}, \quad (2)$$

TABLE 5. Standard thermodynamic quantities. Uncertainties are twice the overall standard deviation of the mean

	$\frac{-\Delta_{\rm c} U_{\rm m}^{\circ}({\rm c})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{-\Delta_{\rm c}H_{\rm m}^{\circ}({\rm c})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{-\Delta_{\rm f}H_{\rm m}^{\circ}({\rm c})}{\rm kJ\cdot mol^{-1}}$	$\frac{\Delta_{\rm sub}H_{\rm m}^{\circ}}{\rm kJ\cdot mol^{-1}}$	$\frac{-\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{\mathbf{a}}H_{\mathbf{m}}^{\circ}}{\mathbf{k}\mathbf{J}\cdot\mathbf{mol}^{-1}}$
Acetylurea Trimethyl isocyanurate	$1495.05 \pm 0.35 \\ 2971.24 \pm 0.55$	$1493.81 \pm 0.35 \\ 2969.38 \pm 0.55$	544.21±0.54 677.92±0.97	$\begin{array}{r} 103.05 \pm 0.67 \\ 88.2 \ \pm 1.2 \end{array}$	$\begin{array}{r} 441.16 \pm 0.86 \\ 589.7 \ \pm 1.5 \end{array}$	5342.9 ± 1.8 9017.1 ± 3.3

 $NH_2CONH_2 + 2CH_3CH_3 = CH_3COCH_3 + 2CH_3NH_2;$

$$\Delta_{\rm r} H_{\rm m}^{\circ} = (150.1 \pm 2.4) \, \rm kJ \cdot mol^{-1}, \quad (3)$$

$$CH_3CONHCONH_2 + 3CH_3CH_3$$

$$= 2CH_3COCH_3 + (CH_3)_2NH + CH_3NH_2;$$

$$\Delta_{\rm r} H_{\rm m}^{\circ} = (202 \pm 3) \, \rm kJ \cdot mol^{-1}, \quad (4)$$

and

$$\underline{\text{CON}(\text{CH}_3)\text{CON}(\text{CH}_3)\text{CON}(\text{CH}_3) + 6\text{CH}_3\text{CH}_3}_{= 3\text{CH}_3\text{COCH}_3 + 3(\text{CH}_3)_3\text{N};}$$
$$\Delta_r H_m^\circ = (369.5 \pm 2.3) \text{ kJ} \cdot \text{mol}^{-1}. \quad (5)$$

Standard molar enthalpies of formation in the gaseous state of compounds other than those under study were taken from reference 13. The standard molar enthalpy of formation in the gaseous state of acetylurea used in this calculation was an estimated value for the trans-trans conformer shown in figure 2. A molecule of this compound takes the *trans-cis* conformation, shown in figure 2, possibly owing to intramolecular N-H--O hydrogen-bond formation, in the crystalline state.⁽¹⁴⁾ A CNDO/2 calculation (fixed molecular geometry)⁽¹⁵⁾ showed that the trans-cis conformer with planar skeleton is more stable than the corresponding trans-trans conformer by 27.8 kJ·mol⁻¹. According to our MINDO/3 calculation using $MOPAC^{(16)}$ with geometry optimization, the standard molar enthalpy of formation in the gaseous state of the most stable distorted trans-cis conformer was $-541.1 \text{ kJ} \cdot \text{mol}^{-1}$, lower than that of the metastable *trans-trans* conformer by 11.1 kJ \cdot mol⁻¹. These calculations suggest that this molecule takes the *trans-cis* conformation also in the gaseous state. Clearly, for a study of the energetics of related molecules, the *trans-trans* conformer with a regular skeleton is more suitable as a reference. However, MINDO/3 is not sufficiently adequate for the reproduction of hydrogen bonds.⁽¹⁷⁾ In fact, the dihedral angle of the $C_1 N_2 C_3 N_4$ skeleton is not 2π but 1.833π and the (N-)H-O distance is 0.2578 nm in the optimized structure, nearly equal to the sum of van der Waals radii of H and O atoms.

Many experimental results show that the N-H--O hydrogen bond energy is in the range 12 to $16 \text{ kJ} \cdot \text{mol}^{-1}$.⁽¹⁸⁾ In this study, the enthalpy difference between the *trans-trans* and *trans-cis* conformers was arbitrarily estimated to be $(14 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$. This means that the standard molar enthalpy of formation in the gaseous state of *trans-trans* acetylurea is estimated to be $-(427 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$.



FIGURE 2. Acetylurea. (a) Trans-cis and (b) trans-trans conformers.

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In the above reactions, CO-N bonds are cleaved and the numbers of cleaved C-N and C-C bonds are equal to those of formed C-N and C-C bonds, respectively ("isodesmic" reaction). In this sense, it is considered that the enthalpy changes might be used as a measure of the magnitude of energetic stabilization of the molecules under study.

The enthalpy change for acetamide is compared with the corresponding values of other normal alkanamides. The latter values were evaluated as enthalpy changes at 298.15 K of the gas-phase reactions:

$$CH_{3}(CH_{2})_{n-1}CONH_{2} + 2CH_{3}CH_{3}$$

= CH_{3}(CH_{2})_{n-1}CH_{3} + CH_{3}COCH_{3} + CH_{3}NH_{2}. (6)

Using standard molar enthalpies of formation in the gaseous state taken from reference 13, enthalpy changes were derived as shown in table 6. They amount to about $81 \text{ kJ} \cdot \text{mol}^{-1}$, independent of the length of the hydrocarbon chain.

The stability of dimethylamine and trimethylamine that appear in reactions (4) and (5), as compared with methylamine, deserves examination. If it is assumed that $E_{\rm m}(\rm C-H) = 412.9 \text{ kJ} \cdot \rm{mol}^{-1}$ and $E_{\rm m}(\rm C-C) = 347.7 \text{ kJ} \cdot \rm{mol}^{-1}$, molar enthalpies of atomization of normal alkanes^(11, 13) can be expressed as follows by the simplest bond-energy scheme:

$$\Delta_{a}H_{m}(C_{k}H_{2k+2}) = (2k+2)E_{m}(C-H) + (k-1)E_{m}(C-C).$$
(7)

Similarly, molar atomization enthalpies of methyl-substituted amines are expressed by the equation:

$$\Delta_{a}H_{m}\{(CH_{3})_{n}NH_{3-n}\} = 3nE_{m}(C-H) + nE_{m}(C-N) + (3-n)E_{m}(N-H).$$
(8)

Using $E_m(C-N) = 297.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $E_m(N-H) = 383.0 \text{ kJ} \cdot \text{mol}^{-1}$ with the value of $E_m(C-H)$ given above, we have 2302 (2302) kJ \cdot mol^{-1}, 3454 (3451) kJ · mol^{-1}, and 4607 (4608) kJ · mol^{-1} for n = 1, 2, and 3, respectively, where parenthesized numbers are the experimental values. Thus, molar atomization enthalpies of methyl-substituted amines are apparently additive with respect to composite bonds. This is the minimum requirement for the use of these compounds as references.

The molar enthalpy change per cleaved CO–N bond amounts to $81.8 \text{ kJ} \cdot \text{mol}^{-1}$, 75.1 kJ·mol⁻¹, 67 kJ·mol⁻¹, and 61.6 kJ·mol⁻¹ for reactions (2), (3), (4), and (5), respectively. This quantity decreases with the elongation of an alternating CO–N chain and that of the six-membered ring is lower than that of any of the linear members.

TABLE 6. Enthalpy changes of reaction (6) at 298.15 K. Normal alkanamides are expressed as $CH_3(CH_2)_{n-1}CONH_2$

n	: 1	2	3	4	5	6	7
$\frac{\Delta_{r} H_{m}^{\circ}}{k J \cdot mol^{-1}}$	(81.8±1.2)	(81.5±1.3)	(79.9±1.6)	(70.6±1.8)	(83.8±2.2)		(81.4±3.6)

To interpret these facts, it seems necessary to analyse the enthalpy changes in more detail. The content of these reactions is four-fold: (a) extinction of π -electron delocalization, (b) rearrangement of C-N and C-C σ -bonds accompanied by the change in σ -bond character

$$\{C(sp^{2})-N+C(sp^{3})-C(sp^{3})=C(sp^{2})-C(sp^{3})+C(sp^{3})-N\},\$$

(c) change in the strength of C–O σ -bonds without change in the bond character, and (d) contributions from additional stabilization and/or destabilization, if any, of relevant species.

Theoretical analysis along the above-mentioned line of extensive thermochemical quantities of aliphatic compounds with alternately adjacent carbonyl groups and nitrogen atoms including the present ones is reported elsewhere.⁽¹⁹⁾

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